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(54) Title: POLYETHYLENE BLOW MOLDING COMPOSITION FOR PRODUCING LARGE CONTAINERS

(57) **Abstract:** The invention relates to a polyethylene composition with multimodal molecular mass distribution, which is particularly suitable for the blow molding of large containers with a volume in the range of from 10 to 150 dm^3 (I). The composition has a density in the range of from 0.949 to 0.955g/cm^3 at 23 °C and an $MFI_{190/5}$ in the range of from 0.1 to 0.3 dg/min. It comprises from 38 to 45 % by weight of a low-molecular-mass ethylene homopolymer A, from 30 to 40 % by weight of a high-molecular-mass copolymer B made from ethylene and from another 1-olefin having from 4 to 8 carbon atoms, and from 18 to 26 % by weight of an ultrahigh-molecular-mass ethylene copolymer C.

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Title: Polyethylene blow molding composition for producing large containers

The present invention relates to a polyethylene blow molding composition with multimodal molecular mass distribution, which is particularly suitable for blow molding of large blow moldings with a capacity in the range from 10 to 150 dm^3 (l), and to a process for preparing this blow molding composition in the presence of a catalytic system composed of a Ziegler catalyst and a co-catalyst like triethylaluminum, triisobutylaluminum, alkylaluminumchlorides and alkylaluminumhydrides, by way of a multistage reaction process composed of successive slurry polymerizations. The invention further relates to large containers produced from the blow molding composition by injection blow molding.

Polyethylene is widely used for producing blow moldings of all types requiring a material with particularly high mechanical strength, high corrosion resistance, and absolutely reliable long-term stability. Another particular advantage of polyethylene is that it also has good chemical resistance and is intrinsically a light-weight material.

EP-A-603,935 has previously described a blow molding composition based on polyethylene and having a bimodal molecular mass distribution, and suitable for the production of moldings with good mechanical properties.

US-A 5,338,589 describes a material with even broader molecular mass distribution, prepared using a high-mileage catalyst known from WO 91/18934, in which the magnesium alcoholate is used in the form of a gel-like suspension. Surprisingly, it has been found that the use of this material in moldings permits simultaneous improvement in properties which are usually contrary correlated in semicrystalline thermoplastics, these being stiffness on the one hand and stress-crack resistance and toughness on the other hand.

However, the known bimodal products, in particular, have relatively low melt strength during processing. This means that the extruded parisons frequently break in the molten state, making the extrusion process unacceptably sensitive to processing. In addition, especially when thick-walled containers are being produced, the wall thickness is found to be non-uniform, due to flow of the melt from upper regions into lower regions of the mold.

It is an objective of the present invention, therefore, to develop a polyethylene composition for blow molding which shows a further improvement over all of the known materials in processing by blow molding to produce large blow moldings. In particular, the high melt strength of the composition should permit to run an extrusion process without parison disruption over a long period, and the precisely adjusted swell ratio index of the composition should permit an optimization of wall-thickness control.

We have surprisingly found that this objective is achieved by way of a composition as mentioned at the outset, the characterizing features of which are that it comprises from 38 to 45 % by weight of a low-molecular-mass ethylene homopolymer A, from 30 to 40 % by weight of a high-molecular-mass copolymer B made from ethylene and from another 1-olefin having from 4 to 8 carbon atoms, and from 18 to 26 % by weight of an ultrahigh-molecular-mass ethylene copolymer C, wherein all of the percentage data are based on the total weight of the molding composition.

The invention also relates to a process for preparing this composition in a cascaded slurry polymerization and to a process for producing, from this composition, large containers with a capacity (volume) in the range from 10 to 150 dm^3 (l) and with quite excellent mechanical properties.

The polyethylene composition of the invention has a density in the range of from 0.949 to 0.955 g/cm^3 at 23 °C, and a broad trimodal molecular mass distribution. The high-molecular-mass copolymer B contains only small

amounts of other 1-olefins having from 4 to 8 carbon atoms, namely from 0.1 to 0.2 % by weight. Examples of these co-monomers are 1-butene, 1-pentene, 1-hexene, 1-octene, or 4-methyl-1-pentene. The ultrahigh-molecular-mass ethylene homo- or copolymer C also contains an amount in the range from 2 to 3 % by weight of one or more of the above mentioned co-monomers.

The polymer composition of the invention has a melt flow index ISO 1133 in the range of from 0.1 to 0.3 dg/min, expressed in terms of $MFI_{190/5}$, and in the range of from 4 to 6 dg/min, expressed in terms of $MFR_{190/21.6}$, and a viscosity number VN_{tot} in the range of from 460 to 500 cm^3/g measured to ISO/R 1191 in decalin at 135 °C.

The trimodality is a measure of the position of the centers of gravity of the three individual molecular mass distributions, and can be described with the aid of the viscosity number VN to ISO/R 1191 of the polymers formed in the successive polymerization stages. The relevant band widths for the polymers formed in each of the stages of the reaction are therefore as follows:

The viscosity number VN_1 measured on the polymer after the first polymerization stage is identical with the viscosity number VN_A of the low-molecular-mass polyethylene A and according to the invention is in the range of from 160 to 220 cm^3/g.

The viscosity number VN_2 measured on the polymer after the second polymerization stage is not equal to VN_B of the high-molecular-mass polyethylene B formed in the second polymerization stage, which can only be determined by calculation, but rather represents the viscosity number of the mixture of polymer A and polymer B. According to the invention, VN_2 is in the range of from 250 to 300 cm^3/g.

The viscosity number VN_3 measured on the polymer after the third polymerization stage is not equal to VN_C of the ultra-high-molecular-mass

copolymer C formed in the third polymerization stage, which can only be determined by calculation, but rather represents the viscosity number of the mixture of polymer A, polymer B, and polymer C. According to the invention, VN_3 is in the range from 460 to 500 cm^3/g.

The polyethylene is obtained by polymerizing the monomers in slurry in a temperature range of from 60 to 90 °C, at a pressure in the range of from 0.15 to 1 MPa, and in the presence of a high-mileage Ziegler catalyst composed of a transition metal compound and of an organoaluminum compound. The polymerization is conducted in three stages, i.e. in three stages arranged in series, each molecular mass being regulated with the aid of a hydrogen feed.

The polyethylene composition of the invention may comprise other additives alongside the polyethylene. Examples of these additives are heat stabilizers, antioxidants, UV absorbers, light stabilizers, metal deactivators, compounds which destroy peroxide, and basic co-stabilizers in amounts of from 0 to 10 % by weight, preferably from 0 to 5 % by weight, and also fillers, reinforcing agents, plasticizers, lubricants, emulsifiers, pigments, optical brighteners, flame retardants, antistatics, blowing agents, or a combination of these, in total amounts of from 0 to 50 % by weight, based on the total weight of the mixture.

The composition of the invention is particularly suitable for the blow molding process to produce large containers, by first plastifying the polyethylene composition in an extruder in the temperature range of from 200 to 250 °C and then extruding it through a die into a mold, where it is blown up and cooled and, thus, solidified.

The composition of the invention gives particularly good processing behavior in the blow molding process to produce large blow moldings, such as large containers, because it has a swell ratio index in the range of from 175 to 205 %, and the large blow moldings produced therewith have particularly high mechanical strength because the molding composition of the invention has a

notched impact strength (ISO) in the range of from 30 to 60 kJ/m². The stress-crack resistance (FNCT) is in the range of from 60 to 110 h.

The notched impact strength$_{ISO}$ is measured according to ISO 179-1/1eA / DIN 53453 at 23 °C. The size of the specimen is 10 x 4 x 80 mm, and a V notch is inserted using an angle of 45°, with a depth of 2 mm and with a notch base radius of 0.25 mm.

The stress-crack resistance of the molding composition of the invention is determined by an internal test method and is given in h. This laboratory method is described by M. Fleißner in Kunststoffe 77 (1987), pp. 45 et seq., and corresponds to ISO/CD 16770, which has since come into force. The publication shows that there is a relationship between determination of slow crack growth in the creep test on specimens with a circumferential notch and the brittle section of the long-term internal- and hydrostatic-pressure test to ISO 1167. In ethylene glycol as stress-crack-promoting medium at 80 °C with a tensile stress of 3.5 MPa, the time to failure is shortened due to the shortening of the stress-initiation time by the notch (1.6 mm/razorblade). The specimens are produced by sawing out three specimens of dimensions 10 x 10 mm from a pressed plaque of thickness 10 mm. These specimens are provided with a central notch, using a razorblade in a notching device specifically manufactured for the purpose (see Figure 5 in the publication). The notch depth is 1.6 mm.

Example 1

Ethylene was polymerized in a continuous process in three reactors arranged in series. An amount of 1.0 mol/h of a Ziegler catalyst prepared as specified in WO 91/18934, Example 2, and having the operative number 2.2 in the WO, was fed into the first reactor together with 15 mol/h of triethylaluminum, as well as sufficient amounts of diluent (hexane), ethylene, and hydrogen. The amount of ethylene (= 5.3 t/h) and the amount of hydrogen (= 2.3 kg/h) were adjusted so that the percentage proportion of ethylene and of hydrogen measured in the gas phase of the first reactor were 33 % by volume and 56 % by volume, respectively, and the rest was a mix of nitrogen and vaporized diluent.

The polymerization in the first reactor was carried out at 70 °C.

The slurry from the first reactor was then transferred into a second reactor, in which the percentage proportion of hydrogen in the gas space had been reduced to 16 % by volume, and an amount of 7 kg/h of 1-butene was added to this reactor alongside 4.5 t/h of ethylene. The amount of hydrogen was reduced by way of intermediate H_2 depressurization. 67 % by volume of ethylene, 16 % by volume of hydrogen, and 0.37 % by volume of 1-butene were measured in the gas phase of the second reactor, the rest being a mix of nitrogen and vaporized diluent.

The polymerization in the second reactor was carried out at 85 °C.

The slurry from the second reactor was transferred to the third reactor using further intermediate H_2 depressurization to adjust the amount of hydrogen to < 0.5 % by volume in the gas phase of the third reactor.

An amount of 69 kg/h of 1-butene was added to the third reactor alongside an amount of 2.8 t/h of ethylene. A percentage proportion of 87 % by volume of ethylene, < 0.5 % by volume of hydrogen, and 1.25 % by volume of 1-butene

was measured in the gas phase of the third reactor, the rest being a mix of nitrogen and vaporized diluent.

The polymerization in the third reactor was carried out at 75 °C.

The long-term polymerization catalyst activity required for the cascaded process described above was provided by a high-mileage Ziegler catalyst as described in the WO mentioned at the outset. A measure of the usefulness of this catalyst is its extremely high hydrogen sensitivity and its uniformly high activity over a long time period of from about 1 to 8 h.

The diluent is removed from the polymer slurry leaving the third reactor, and the polymer is dried and then pelletized.

Table 1 shown below gives the viscosity numbers and quantitative proportions w_A, w_B, and w_C of polymer A, B, and C for the polyethylene composition prepared in Example 1.

Table 1

Example	
density [g/cm³]	0.951
$MFI_{190/5}$ [dg/min]	0.20
$MFR_{190/21.6}$ [dg/min]	4.6
W_A [% by weight]	42
W_B [% by weight]	36
W_C [% by weight]	22
VN_1 [cm³/g]	200

VN_2 [cm^3/g]	270
VN_{tot} [cm^3/g]	480
SR [%]	190
FNCT [h]	80
NIS_{ISO} [kJ/m^2]	40

The abbreviations for physical properties in Table 1 have the following meanings:

- SR (= swell ratio) in [%] measured in a high-pressure capillary rheometer at a shear rate of 1440 s^{-1}, in a 2/2 round-section die with conical inlet (angle = 15°) at 190 °C.

- FNCT = stress-crack resistance (Full Notch Creep Test) tested using the internal test method of M. Fleißner, in [h],

- NIS_{ISO} = notched impact strength measured to ISO 179-1/1eA / DIN 53453 in [kJ/m^2] at 23 °C.

* * * * *

We claim

1. A polyethylene composition with multimodal molecular mass distribution, which has a density in the range of from 0.949 to 0.955 g/cm³ at 23 °C and a $MFI_{190/5}$ in the range from 0.1 to 0.3 dg/min or a $MFI_{190/21.6}$ in the range of 4 to 6 dg/min, and which comprises from 38 to 45 % by weight of a low-molecular-mass ethylene homopolymer A, from 30 to 40 % by weight of a high-molecular-mass copolymer B made from ethylene and from another 1-olefin having from 4 to 8 carbon atoms, and from 18 to 26 % by weight of an ultrahigh-molecular-mass ethylene copolymer C, wherein all of the percentage data are based on the total weight of the molding composition.

2. A polyethylene composition as claimed in claim 1, wherein the high-molecular-mass copolymer B contains small proportions of from 0.1 to 0.2 % by weight of co-monomer having from 4 to 8 carbon atoms, based on the weight of copolymer B, and wherein the ultrahigh-molecular-mass ethylene copolymer C contains an amount in the range from 2 to 3 % by weight of co-monomers, based on the weight of copolymer C.

3. A polyethylene composition as claimed in claim 1 or 2, which, as co-monomer, contains 1-butene, 1-pentene, 1-hexene, 1-octene, 4-methyl-1-pentene, or a mixture of these.

4. A polyethylene composition as claimed in one or more of claims 1 to 3, which has a viscosity number VN_{tot} in the range of from 460 to 500 cm³/g measured to ISO/R 1191 in decalin at 135 °C.

5. A polyethylene composition as claimed in one or more of claims 1 to 4, which has a swell ratio index in the range of from 175 to 205 %, and a notched impact strength (ISO) in the range of from 30 to 60 kJ/m², and a stress-crack resistance (FNCT) in the range of from 60 to 110 h.

6. A process for producing a polyethylene composition as claimed in one or more of claims 1 to 5, in which the monomers are polymerized in slurry in a temperature range of from 60 to 90 °C at a pressure in the range of from 0.15 to 1 MPa, and in the presence of a high-mileage Ziegler catalyst composed of a transition metal compound and of an organoaluminum compound, which comprises conducting polymerization in three stages, where the molecular mass of the polyethylene prepared in each stage is regulated with the aid of hydrogen.

7. A process as claimed in claim 6, wherein the hydrogen concentration in the first polymerization stage is adjusted so that the viscosity number VN_1 of the low-molecular-weight polyethylene A is in the range of from 160 to 220 cm³/g.

8. A process as claimed in claim 6 or 7, wherein the hydrogen concentration in the second polymerization stage is adjusted so that the viscosity number VN_2 of the mixture of polymer A and polymer B is in the range of from 250 to 300 cm³/g.

9. A process as claimed in any of claims 6 to 8, wherein the hydrogen concentration in the third polymerization stage is adjusted so that the viscosity number VN_3 of the mixture of polymer A, polymer B, and polymer C is in the range of from 460 to 500 cm³/g.

10. The use of a polyethylene composition as claimed in one or more of claims 1 to 5 for producing large blow moldings, such as containers, with a capacity in the range of from 10 to 150 dm³ (l), wherein the polyethylene

molding composition is first plasticized in an extruder in a temperature range of from 200 to 250 °C and is then extruded through a die into a blow mold, where it is blown up and then cooled and solidified.

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L23/04 C08F297/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 199 45 980 A (ELENAC GMBH) 29 March 2001 (2001-03-29) the whole document	1-10
X	US 4 536 550 A (IKEGAMI TADASHI ET AL) 20 August 1985 (1985-08-20) the whole document	1-10
X	US 4 336 352 A (SAKURAI HISAYA ET AL) 22 June 1982 (1982-06-22) the whole document	1-10
A	US 6 242 548 B1 (KASPAR HARALD ET AL) 5 June 2001 (2001-06-05) the whole document	1-10

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 603 935 A (SOLVAY) 29 June 1994 (1994-06-29) cited in the application the whole document _____	1-10

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 19945980 A	29-03-2001	DE 19945980 A1	29-03-2001
		AT 244264 T	15-07-2003
		AU 769434 B2	29-01-2004
		AU 7001700 A	30-04-2001
		BR 0014232 A	04-06-2002
		CA 2387708 A1	05-04-2001
		CN 1376170 T	23-10-2002
		DE 50002772 D1	07-08-2003
		WO 0123446 A1	05-04-2001
		EP 1228101 A1	07-08-2002
		JP 2003510429 T	18-03-2003
US 4536550 A	20-08-1985	JP 1012777 B	02-03-1989
		JP 1612249 C	30-07-1991
		JP 59196345 A	07-11-1984
		JP 1012778 B	02-03-1989
		JP 1612250 C	30-07-1991
		JP 59196346 A	07-11-1984
		JP 60036546 A	25-02-1985
		JP 1012781 B	02-03-1989
		JP 1612255 C	30-07-1991
		JP 60036547 A	25-02-1985
		CA 1218181 A1	17-02-1987
		DE 3470168 D1	05-05-1988
		EP 0129312 A1	27-12-1984
US 4336352 A	22-06-1982	JP 1282819 C	27-09-1985
		JP 56032506 A	02-04-1981
		JP 59010724 B	10-03-1984
		BE 884866 A1	16-12-1980
		BR 8005307 A	04-03-1981
		CA 1138148 A1	21-12-1982
		DE 3031540 A1	09-04-1981
		FR 2463791 A1	27-02-1981
		GB 2056996 A ,B	25-03-1981
		IT 1193551 B	08-07-1988
		NL 8004745 A ,C	26-02-1981
US 6242548 B1	05-06-2001	AU 6044399 A	05-12-2000
		CA 2372222 A1	23-11-2000
		EP 1185583 A1	13-03-2002
		WO 0069969 A1	23-11-2000
EP 0603935 A	29-06-1994	BE 1006439 A3	30-08-1994
		AT 191724 T	15-04-2000
		AU 670976 B2	08-08-1996
		AU 5249693 A	30-06-1994
		BR 9305106 A	28-06-1994
		CZ 9302853 A3	13-07-1994
		DE 69328345 D1	18-05-2000
		DE 69328345 T2	07-12-2000
		EP 1364971 A2	26-11-2003
		EP 0603935 A1	29-06-1994
		EP 0940411 A2	08-09-1999
		ES 2147192 T3	01-09-2000
		FI 935772 A	22-06-1994
		GR 3033922 T3	30-11-2000
		HU 66491 A2	28-11-1994

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0603935 A		NO 934729 A	22-06-1994
		PL 301589 A1	27-06-1994
		PT 603935 T	31-10-2000
		US 6344522 B1	05-02-2002
		US 6407185 B1	18-06-2002
		US 6136924 A	24-10-2000
		ZA 9309588 A	11-08-1994